

Performance Characteristics of Lithium Ion Cells For Low Temperature Applications

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Several of NASA's future Planetary Exploration (specifically Mars) missions will require rechargeable batteries of high specific energy and energy density and more importantly of good low temperature performance. Li ion cells have shown considerable promise, not withstanding their relatively poor low temperature performance. The cell component mainly responsible for the low temperature performance is the electrolyte solution. Typical electrolyte solutions in the Li ion cells contain lithium salts (LiPF_6) dissolved in mixtures of alkyl carbonates, which enable the formation of surface films (on carbon anodes)¹ of desired stability and ionic conductivity, e.g., ethylene carbonate (EC) or propylene carbonate (PC) and dimethyl carbonate (DMC) or diethyl carbonate (DEC) or ethyl methyl carbonate (EMC). In our earlier studies,² we have examined various ternary solvent formulations, chosen based on the physicochemical properties of the additives, for improved low temperature performance. However, some of these solvent additives may be reactive towards the anode, which poses uncertainty on their stability under ambient conditions. Since, the intended application requires long cycle life at room temperature, in addition to improved low temperature performance, we started to reexamine the carbonate based solvents and mixtures thereof. Here, we report our recent studies aimed at identifying the optimum composition of the carbonate-based solvent mixtures for improving various attributes, including low temperature performance of the Li ion cells.

The studies are mostly focussed on graphite as the anode material, which warrants the electrolyte to be based on ethylene carbonate rather than propylene carbonate. The electrolyte combinations investigated consist of low EC content (30-35 %) and varying proportions of DMC and DEC and would therefore reflect the effects of the ratio of DMC:DEC. Specifically, the electrolyte mixtures include 1) EC:DMC 30:70, 2) EC:DEC 30:70 and 3) EC:DMC:DEC: 1:1:1, respectively.

Detailed conductivity measurements of the corresponding solutions have been carried out at various temperatures from -60° to 25° C (Table-1). At room temperatures, solutions with high DMC content showed the highest conductivity. On the other hand, at low temperatures, ternary solutions displayed the highest

conductivities. The conductivities of binary solutions and mixtures with high EC content, decrease sharply below -20°C . The improved conductivity of the ternary system over the binary electrolytes at low temperatures is due to the synergistic effect of having EC (possesses good coordinating ability and high dielectric constant), DEC (lowers the melting point of the medium), and DMC (lowers the viscosity of the system) present in the proper proportions and the fact that the lithium coordination complexes formed in ternary solutions are more disordered allowing higher ionic mobility.

Similar to the room temperature conductivity, solutions with high DMC proportions showed less irreversible capacity and higher reversible capacity with graphite anodes, compared to DEC-based solutions. This could be attributed to more favorable (anode) surface films in DMC-based solutions, as evident from the *ac* impedance data. Ternary solutions showed intermediate behavior.

Consistent with the low temperature conductivity data, the cells containing ternary solutions outperform the binary solutions at low temperatures (Fig. 1). As much as 85% of the room temperature capacity is realizable at -20°C , and about 60 % available at low rate (C/10) at -30°C with the ternary electrolyte.

Capacity retention during cycling at ambient temperatures is also impressive with the ternary electrolyte (Fig. 2). Because of the higher initial capacity the capacity of the cell with ternary electrolyte is higher than the cell with DMC-rich electrolyte over 600 cycles, despite a low capacity fade for the latter. The self-discharge characteristics are expectedly better with the DMC-rich electrolyte, because of the superior surface film.

Encouraged by the above, we have proceeded to demonstrate the benefits of the ternary electrolyte in D-size cells. The capacity of the D-size cells, fabricated at Wilson Greatbatch Ltd., range from 3.6 –3.9 Ah (Fig.3). In this paper, we report the performance characteristics of these cells under various experimental conditions, including conditions pertinent to Mars 2001Rover, which is baselined on the Li ion batteries.

ACKNOWLEDGMENTS

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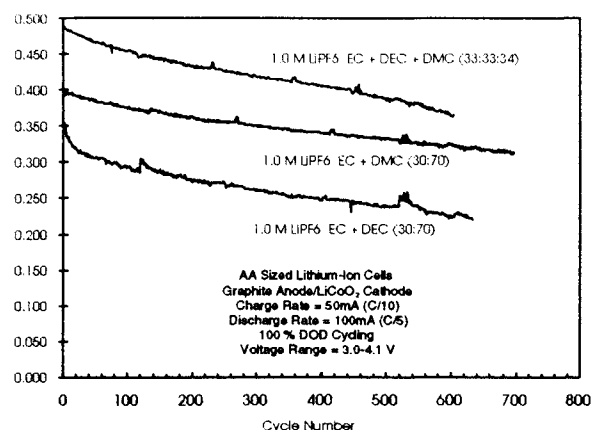


Fig. 3 Room temperature cycle life performance of graphite-based AA size Li-ion cells. Cells were charged at rate of 50mA (~C/10) and discharged at a rate of 100mA (~C/5).

Electrolyte Concentration	Solvent System	Conductivity (mS/cm)					
		-60°	-40°	-20°	0°C	R.T.	
1.0 M LiPF ₆	EC + DMC (30:70)		Fr.	1.9	7.1	12.2	
1.0 M LiPF ₆	EC + DEC (30:70)	Fr.	0.66	1.9	4.0	7.5	
1.0 M LiPF ₆	EC + DEC + DMC (1:1:1)	0.02	1.01	2.9	5.6	9.7	

Table.1. Specific conductivity of EC- and PC-based electrolytes from -60° to 25°C.

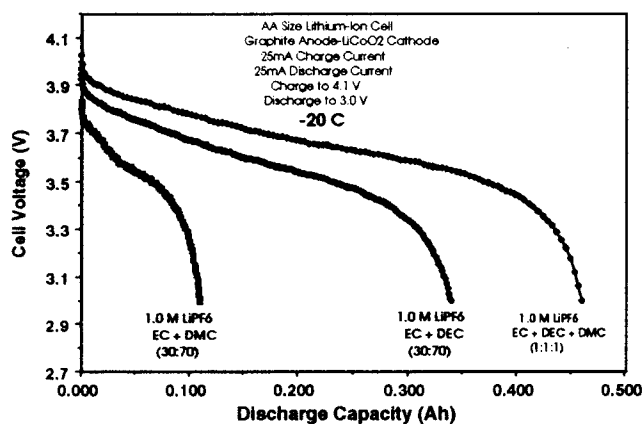


Fig. 2. Comparison of the discharge capacities of graphite-based JPL/WGL AA-size lithium-ion cells at -20°C as a function of electrolyte.

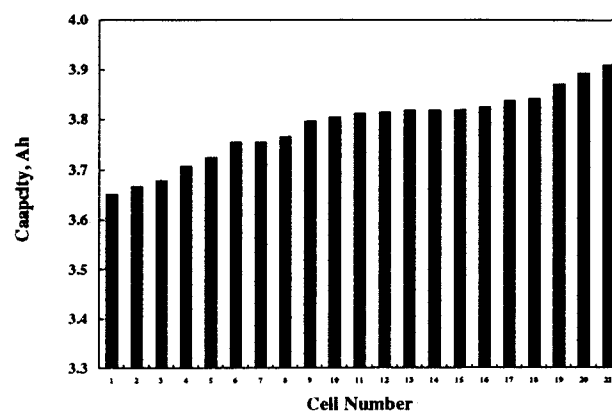


Fig. 4 Initial capacity of JPL D-size Li ion cells during conditioning cycles.